(19) JAPANESE PATENT OFFICE (JP)

(12) **Patent Gazette (B2)**

(11) Japanese Patent (Tokkyo) No. **3180407** **(P3180407)**

(45) Publication Date: June 25, 2001

(24) Registration Date: April 20, 2001

(51) Int. Cl.[7]	Classification Symbols	FI	
C 08 G 64/08		C 08 G 64/08	
B 29 C 45/00		B 29 C 45/00	
C 08 J 5/00	CFD	C 08 J 5/00	CFD
// B 29 K 69:00			
C 08 L 69:00			

Number of Claims: 6 (Total of 8 pages)

(21) Application No.: No. 4–11161

(22) Filing Date: January 24, 1992

(65) Japanese Unexamined Patent Application No.: 5–202182

(43) Disclosure Date: August 10, 1993

Examination Request Date: January 7, 1999

(73) Patentee: 000004466
Mitsubishi Gas Chemical Company, Inc.
5–2 Marunouchi 2–chome, Chiyoda-ku, Tokyo

(72) Inventor: Noriyoshi Ogawa
c/o Mitsubishi Gas Chemical Company, Inc., Osaka Factory; 12 Kamisu-cho, 2–chome, Toyonaka-shi, Osaka-fu

(72) Inventor: Satoshi Kanayama
c/o Mitsubishi Gas Chemical Company, Inc., Osaka Factory; 12 Kamisu-cho, 2–chome, Toyonaka-shi, Osaka-fu

Examiner: Satoshi Morikawa

(56) Cited Literature: International Publication 91/885 (WO, A1)

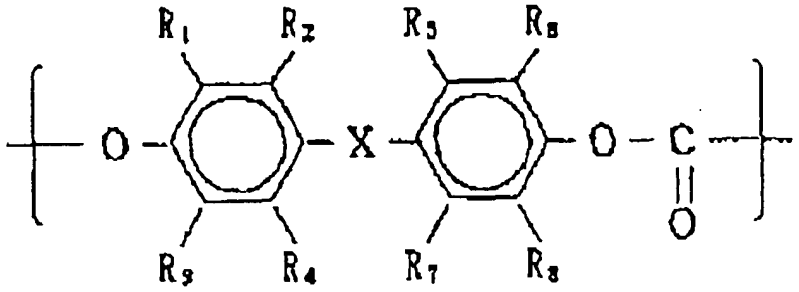
(58) Field of Search (Int. Cl.[7], DB Nomenclature)
C08G 64/00 - 64/42
CA (STN)
REGISTRY (STN)

(54) [Title of the Invention] Polycarbonate Copolymer Injection Molding

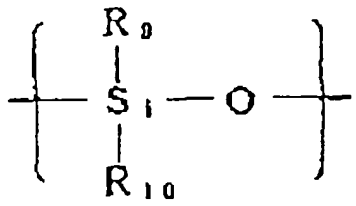
(57) [Claims]

[Claim 1] A molding, obtained by the injection molding of a polycarbonate-polysiloxane random copolymer whose structural units are expressed by General Formulas (A) and (B) below and in which the proportion of structural units expressed by (B) is 0.1–20 wt%, wherein said polycarbonate copolymer injection molding is such that the concentration of structural units (B) in a surface layer less than 50 Å deep from the surface of the molding is at least twice the concentration of structural units (B) in a core layer with a depth of 50 Å or greater.

[Chemical Formula 1]



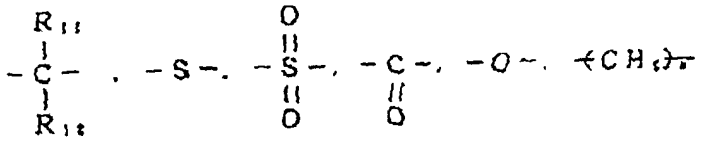
(A)



(B)

(where R1 to R8 are each a hydrogen, a halogen, or an optionally substituted alkyl or aryl group; R9 and R10 are each a hydrogen, a halogen, or an optionally substituted alkyl or aryl group; X is

[Chemical Formula 2]



R_{11} and R_{12} are each a hydrogen, a halogen, or an optionally substituted alkyl or aryl group (R_{11} and R_{12} are groups that link together to form a carbon ring or hetero ring); and *a* is an integer of 1 or greater).

[Claim 2] A molding as defined in Claim 1, wherein the said molding has a thickness of 0.4–10.0 μm.

[Claim 3] A molding as defined in Claim 1, wherein the proportion of structural units (B) in the polycarbonate-polysiloxane random copolymer is 1–20 wt%, and the concentration of structural units (B) in a surface layer with a depth of less than 50 Å is 2–100 wt%.

[Claim 4] A molding as defined in Claim 1, wherein the viscosity-average molecular weight of the polycarbonate-polysiloxane random copolymer is 15,000–100,000.

[Claim 5] A molding as defined in Claim 1, wherein the structural units (A) are derived from a dihydric phenol selected from the group consisting of 2,2-bis(4-hydroxyphenyl)propane and 1,1-bis(4-hydroxyphenyl)cyclohexane.

[Claim 6] A molding as defined in Claim 1, wherein the structural units (B) are α,ω-bis[3-(*o*-hydroxyphenyl)propyl]-polydimethylsiloxane.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a polycarbonate injection molding characterized by improved lubricity or abrasion resistance, and more particularly to a polycarbonate-polysiloxane random copolymer molding in which the concentration of siloxane structural units in the surface layer is higher than in the core layer.

[0002]

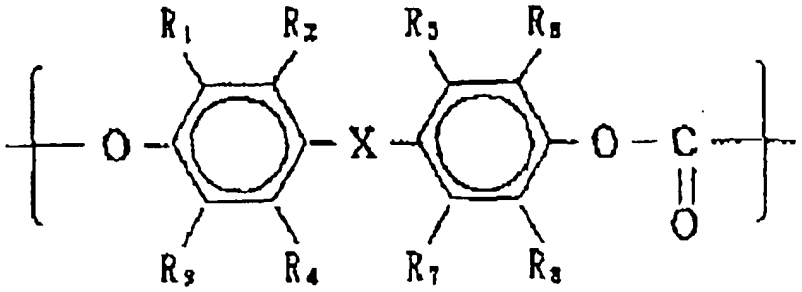
[Prior Art] Silicone oil or polysiloxane blends are commonly added to endow polycarbonates with lubricity, abrasion resistance, and other improved surface properties. Making a small addition fails to provide adequate surface modification, however. Making a large addition has an adverse effect on compatibility with polycarbonates, so the resulting moldings become clouded, acquire inferior mechanical characteristics (flexural, tensile, and the like), and are incapable of preserving their surface characteristics due to abrasion or shedding during extended use.

[0003]

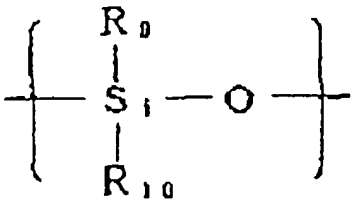
[Means Used to Solve the Above-Mentioned Problems] The present invention was devised in order to address these problems. Specifically, the present invention resides in a molding obtained by the injection molding of a polycarbonate-polysiloxane random copolymer whose structural units are expressed by General Formulas (A) and (B) below and in which the proportion of structural units expressed by (B) is 0.1–20 wt%, wherein this polycarbonate copolymer injection molding is such that the concentration of structural units (B) in a surface layer less than 50 Å deep from the surface of the molding is at least twice the concentration of structural units (B) in a core layer with a depth of 50 Å or greater.

[0004]

[Chemical Formula 3]



(A)

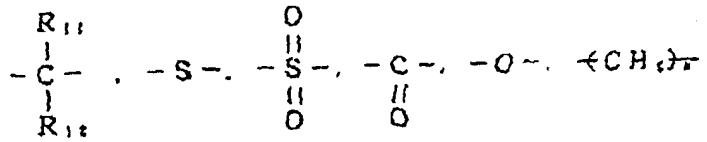


(B)

[0005] (where R1 to R8 are each a hydrogen, a halogen, or an optionally substituted alkyl or aryl group; R9 and R10 are each a hydrogen, a halogen, or an optionally substituted alkyl or aryl group; X is

[0006]

[Chemical Formula 4]

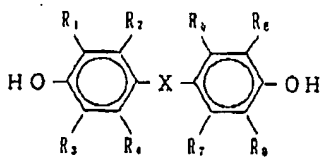


[0007] R_{11} and R_{12} are each a hydrogen, a halogen, or an optionally substituted alkyl or aryl group (R_{11} and R_{12} are groups that link together to form a carbon ring or hetero ring); and *a* is an integer of 1 or greater). The proportion of structural units expressed by (B) should preferably be 1–20 wt%. Structural units (A) and (B) are randomly repeating units.

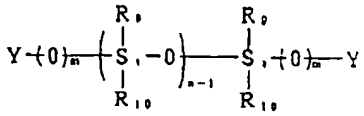
[0008] The structure of the present invention will now be described in detail. The polycarbonate resin used in the present invention can be obtained by copolymerizing phosgene, a carbonate ester, or chloroformate with a dihydric phenol expressed by General Formula (1) below and a polysiloxane expressed by General Formula (2) below.

[0009]

[Chemical Formula 5]



(1)



(2)

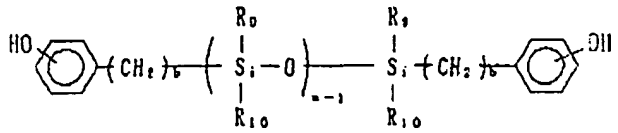
[0010] (In General Formula (1), X and R_1–R_8 are the same as in General Formula (A), and *n* is an integer from 1 to 1000. In General Formula (2), R_9 and R_{10} are each a hydrogen, a halogen, or an optionally substituted alkyl or aryl group; Y is a halogen, $-R_{13}OH$, $-R_{13}COOH$, $-R_{13}NH_2$, $-R_{13}NH_2$, or –SH; R_{13} is a straight, branched, or cyclic alkylidene group, aryl-substituted alkylidene group, or aryl group; R_{14} is an alkyl, alkenyl, aryl, or aralkyl group; and *m* is 0 or 1.) The product is a polycarbonate-polysiloxane copolymer in which the proportion of structural units expressed by General Formula (B) is 0.1–20 wt%. Lower transparency results if the proportion of structural units expressed by General Formula (B) exceeds 20 wt%. The proportion of the structural units expressed by (B) should preferably be 1.0 wt% or greater. When this proportion is less than 1.0 wt%, the concentration of polysiloxane on the surface is insufficient, and surface characteristics tend to deteriorate. The viscosity-average molecular weight of the copolymer should preferably be 15,000–50,000. A viscosity-average molecular weight less than 15,000 yields inferior molding strength, whereas a molecular weight in excess of 50,000 tends to have an adverse effect on productivity.

[0011] Examples of the dihydric phenols expressed by General Formula (1) and used as starting materials for the co-polycarbonate resin of the present invention include bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfoxide, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)ketone, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A; BPA), 2,2-bis(4-hydroxyphenyl)butane, 1,1-bis(4-hydroxyphenyl)cyclohexane (bisphenol Z; BPZ), 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane, 2,2-bis(4-hydroxy-3-bromophenyl) propane, 2,2-bis(4-hydroxy-3-chlorophenyl)propane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, and bis(4-hydroxyphenyl)diphenylmethane. Of these, 2,2-bis(4-hydroxyphenyl)propane and 1,1-bis(4-hydroxyphenyl)cyclohexane are particularly preferred.

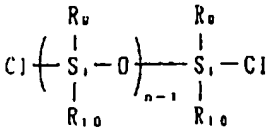
[0012] The following are examples of polysiloxanes expressed by General Formula (2) above.

[0013]

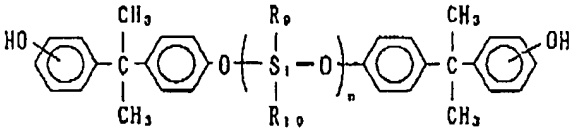
[Chemical Formula 6]



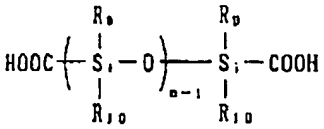
(3)



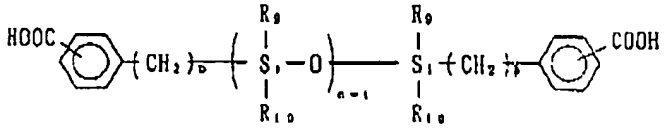
(4)



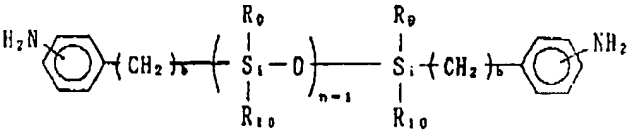
(5)



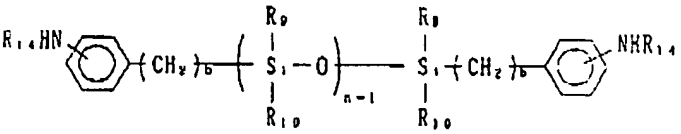
(6)



(7)



(8)



(9)

[0014] (In General Formulas (3) to (9), R_9 and R_{10} are each a hydrogen, a halogen, or an optionally substituted alkyl or aryl group in the same manner as in General Formula (1); R_{14} is an alkyl, alkenyl, aryl, or aralkyl group in the same manner as the Y in General Formula (2); n is an integer from 1 to 1000; and b is a positive integer). Of these, α,ω-bis[3-(*o*-hydroxyphenyl)propyl]-polydimethylsiloxane is particularly preferred.

[0015] A dihydric phenol expressed by General Formula (2) above can be readily produced by causing a phenol (preferably vinyl phenol, allyl phenol, or isopropenyl phenol) having olefinic unsaturated carbon-carbon bonds to undergo a hydrosilanation reaction with the ends of a polysiloxane chain having a specific degree of polymerization n.

[0016] End blockers or molecular weight adjustors are commonly used to produce a polycarbonate. The end blockers may be compounds having monovalent phenolic hydroxyl groups. Such compound include long-chain alkyl phenols, aliphatic carboxylic chlorides, aliphatic carboxylic acids, hydroxybenzoic alkyl esters, hydroxyphenyl alkyl acid esters, and alkyl ether phenols in addition to the usual phenol, *p*-tertiary butyl phenol, tribromophenol, and the like. These should be used in an amount of 0.5–100 mol, and preferably 2–50 mol, per 100 mol of the combined amount of dihydric phenol

compounds. It is apparent that two or more of these compounds may be used jointly. Branching agents may also be used together with the aforementioned dihydric phenol compounds in an amount of 0.01–3 mol%, and particularly 0.1–1.0 mol%, in which case a branched polycarbonate is obtained. Examples of such branching agents include phloroglycin, 2,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)heptene-3, 4,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)heptene-2, 1,3,5-tri(2-hydroxyphenyl)benzene, 1,1,1-tri(4-hydroxyphenyl)ethane, 2,6-bis(2-hydroxy-5-methylbenzyl)-4-methylphenol, α,α',α,"-tri(4-hydroxyphenyl)-1,3,5-triisopropylbenzene, and other polyhydroxy compounds, as well as 3,3-bis(4-hydroxyaryl)oxyindole (isatin bisphenol), 5-chloroisatin, 5,7-dichloroisatin, and 5-bromoisatin.

[0017] Various known additives conventionally used with polycarbonate resins may also be optionally added to the polycarbonate resin used in the present invention. Examples of such additives include reinforcing materials, fillers, stabilizers, UV absorbers, antistatic agents, lubricants, release agents, dyes, pigments, fire retardants, and elastomers (added to achieve better impact resistance).

[0018] The injection molding of the present invention can be molded by a common injection molding technique. When a PC-polysiloxane copolymer is discharged, the polysiloxane is caused to migrate to the surface by an injection molding technique in which shear is applied, and the siloxanes are concentrated on the extreme surface. The shear rate should preferably be 5×10^3 to 5×10^6 (1/sec). A shear rate below 5×10^3 (1/sec) fails to yield a sufficient siloxane concentration, whereas a shear rate in excess of 5×10^6 (1/sec) cannot provide the required fluidity and tends to impair injection. The resin temperature should preferably be 250–340°C because of considerations related to heat resistance and fluidity.

[0019] The thickness of the injection molding should preferably be 0.4–10.0 mm under normal conditions. A thickness less than 0.4 mm yields inadequate molding strength, whereas a thickness greater than 10 mm impairs moldability. In the molding of the present invention, the concentration of structural units (B) in a surface layer less than 50 Å deep from the surface of the molding is at least twice the concentration of structural units (B) in a core layer with a depth of 50 Å or greater. When the proportion of structural units (B) is 1–20 wt%, the concentration of structural units (B) in the surface layer should preferably fall within a range of 2–100 wt%.

[0020] The composition of the surface layer with a depth of less than 50 Å in the polycarbonate-polysiloxane copolymer injection molding of the present invention was analyzed by ESCALAB MK2 (manufactured by V. G. Scientific) for C-1S, O-1S, and Si-2P. The following peaks were detected for C (carbon): peaks ascribed to C-C, C=C, C-H, and C-Si; peaks ascribed to C-O at 286.1–286.2 eV; peaks ascribed to carbonate bonds (OCOO) at 290.5–290.7 eV; and shake-up satellite peaks ascribed to the π–π* transitions in unsaturated bonds at 291.7–292.3 eV. The following peaks were detected for O (oxygen): peaks ascribed to C=O and Si-O at 532.2–532.3 eV, and peaks ascribed to C-O at 533.9–534.0 eV. A peak ascribed to –O-Si$(CH_3)_2$-O- (siloxane) at 102 eV was detected for Si (silicon). Although the depth measured by ESCA varied with the type of atom and the electron energy, the mean free path for O and Si was 20 Å or less at 100–600 eV, and hardly any atoms were detected at a depth of 50 Å or greater. Consequently, the concentration of siloxanes in a surface layer whose depth is less than 50 Å was measured by ESCA. Core layers with a depth of 50 Å or greater from the surface layer were analyzed by a method in which the surface was etched with argon to remove 50 Å from the surface, the remaining portion was measured, and the results were compared.

[0021]

[Working Examples]

Working Example 1

A solution was prepared by adding the following components to 580 L of a 8.8% (W/V) aqueous solution of sodium hydroxide: 91.2 kg of bisphenol A (BPA), 5.95 kg of a dihydric phenol expressed by General Formula (3) above (where R_9 and R_{10} were methyl groups, *ortho* bonds were formed at $n = 41$ and $b = 3$, and the amount was selected such that structural units (B) constituted 5 wt%), and 100 g of hydrosulfite. Methyl chloride (360 L) was added thereto, the system was stirred while kept at 15°C, *p-t*-butylphenol (PTBP; 1.44 kg) was added in the process, and phosgene (53.0 kg) was then blown in over a period of 60 minutes. The blowing was followed by vigorous stirring to emulsify the reaction solution, and the emulsification was followed by the addition of triethylamine (100 mL), agitation for about 1 hour, and polymerization. The polymerization solution was separated into an aqueous layer and an organic layer, the organic layer was neutralized with phosphoric acid, the product was repeatedly washed with water until the pH of the wash liquor became neutral, isopropanol (470 L) was then added, and the polymer was precipitated. The precipitate was filtered and dried, yielding a white pulverulent polycarbonate-polysiloxane copolymer (PC-Si) resin. The PC-Si resin thus obtained was fashioned into an injection molding with a length of 127 mm, a width of 12.7 mm, and a thickness of 3.2 mm at a nozzle diameter of 3 mm, a resin temperature of 300°C, a screw speed of 50 rpm (screw diameter: 45 mm), an injection speed of 1.6 cm/sec, a maximum injection pressure of 1400 kg/cm^2, a holding pressure of 1000 kg/cm^2, and an injection time of 15 sec in an injection molding machine manufactured by Meiki. The shear rate was 9.8×10^3 (1/sec); the injection rate, 26 cc/sec. The shear rate was calculated using the following formula.

$r\omega a$ (shear rate) $= 4Q/\pi R^3$, where

Q = Capillarity-induced volume outflow (cm^3)

R = Capillary radius (cm)

The resulting injection molding was then tested as described below. The results are shown in Table 1.

[0022] The above-described ESCA was used to quantify (for C-1S, O-1S, and Si-2P) the siloxane concentration (wt%) of a surface layer whose depth was less than 50 Å from the surface of the injection molding and to quantify the siloxane concentration (wt%) of a core layer with a depth of 50 Å or greater. The randomness of the molding was evaluated by detecting the presence of filamentous nonuniformities (irregularities) by TEM observations. In Table 1, "×" and "O" are used to designate the presence and absence, respectively, of such nonuniformities. The abrasion resistance of moldings was evaluated by measuring abrasion (in mg) with a Taber abrasion tester (load: 1 kg; CS-17

wheels; toluene atmosphere;24 hr).

[0023] Working Example 2

The same procedures as in Working Example 1 were performed except that bisphenol Z (BPZ) was used in an amount of 107.2 kg instead of the BPA. The results are shown in Table 1.

[0024] Working Example 3

The same procedures as in Working Example 1 were performed except that a concentration of 1 wt% was set for the structural units (B) in the dihydric phenol of General Formula (3) above (R_9 and R_{10} were methyl groups, and *ortho* bonds were formed at $n = 41$ an $b = 3$). The results are shown in Table 1.

[0025] Working Example 4

The same procedures as in Working Example 1 were performed except that a concentration of 20 wt% was set for the structural units (B) in the dihydric phenol of General Formula (3) above (R_9 and R_{10} were methyl groups, and *ortho* bonds were formed at $n = 41$ an $b = 3$). The results are shown in Table 1.

[0026] Working Example 5

The same procedures as in Working Example 1 were performed except that the dihydric phenol of General Formula (3) above was a compound in which R_9 and R_{10} were methyl groups and *para* bonds were formed at $n = 41$ an $b = 2$. The results are shown in Table 1.

[0027] Working Example 6

The same procedures as in Working Example 1 were performed except that the dihydric phenol of General Formula (3) above was a compound in which R_9 and R_{10} were methyl groups and *ortho* bonds were formed at $n = 101$ an $b = 3$. The results are shown in Table 1.

[0028] Working Example 7

The same procedures as in Working Example 1 were performed except that the dihydric phenol of General Formula (3) above was a compound in which R_9 was a methyl group, R_{10} was a phenyl group, and *ortho* bonds were formed at $n = 41$ an $b = 3$. The results are shown in Table 1.

[0029] Working Example 8

The same procedures as in Working Example 1 were performed except that the dihydric phenol was a dihydric phenol of General Formula (4) above, R_9 and R_{10} were methyl groups, and $n = 41$. The results are shown in Table 1.

[0030] Comparative Example 1

The same procedures as in Working Example 1 were performed except that the dihydric phenol containing the siloxanes of General Formula (2) was dispensed with completely. The results are shown in Table 1.

[0031] Comparative Example 2

The same procedures as in Working Example 2 were performed except that the dihydric phenol containing the siloxanes of General Formula (2) was dispensed with completely. The results are shown in Table 1.

[0032] Comparative Example 3

The same procedures as in Working Example 1 were performed except that a dihydric phenol of General Formula (3) for which R_9 and R_{10} were methyl groups and *ortho* bonds were formed at $n = 41$ and $b = 3$ was used such that the content of structural units (B) in the copolymer was 0.09 wt%. The results are shown in Table 1.

[0033] Comparative Example 4

The same procedures as in Working Example 1 were performed except that a dihydric phenol of General Formula (3) for which R_9 and R_{10} were methyl groups and *ortho* bonds were formed at $n = 41$ and $b = 3$ was used such that the content of structural units (B) in the copolymer was 25 wt%. The results are shown in Table 1.

[0034] Comparative Example 5

A dihydric phenol of General Formula (3) for which R_9 and R_{10} were methyl groups and *ortho* bonds were formed at $n = 41$ and $b = 3$ was blended with the polycarbonate of Comparative Example 1 such that the proportion of structural units (B) was 5 wt%. The results are shown in Table 1.

Table 1

	monomer					viscosity-average molecular weight	film characteristics			
	phenol of formula (A)*1 wt%		siloxane of formula (B)*2 wt%				siloxane concentration siloxane concentration of surface layer with depth of less than 50 Å (wt%)	randomness	abrasion resistance pencil hardness	abrasion, mg
Example 1	BPA	95.0	(1)	5.0	3.0×10^4	14	O	2H	13
Example 2	BPZ	95.0	(1)	5.0	3.3×10^4	15	O	2H	13
Example 3	BPA	99.0	(1)	1.0	3.0×10^4	5	O	H	18
Example 4	BPA	80.0	(1)	20.0	3.2×10^4	43	O	3H	10
Example 5	BPA	95.0	(2)	5.0	3.0×10^4	12	O	2H	14
Example 6	BPA	95.0	(3)	5.0	3.0×10^4	15	O	2H	15
Example 7	BPA	95.0	(4)	5.0	3.3×10^4	12	O	2H	17
Example 8	BPA	95.0	(5)	5.0	3.0×10^4	16	O	2H	14
Comparison 1	BPA	100.0	–	0.0	3.0×10^4	-	O	HB	32
Comparison 2	BPZ	100.0	–	0.0	3.2×10^4	-	O	H	23
Comparison 3	BPA	99.91	(1)	0.09	3.0×10^4	0.5	O	H	26
Comparison 4	BPA	75.0	(1)	25.0	3.4×10^4	56	×	3H	10
Comparison 5	BPA	95.0	(1)*3	5.0	3.0×10^4	9	×	H	25

*1 BPA: bisphenol A, BPZ: bisphenol Z

*2 (1) Polysiloxane of General Formula (3) in which R_9 and R_{10} ar methyl groups, and *ortho* bonds are formed at $n = 41$ and $b = 3$

[0035]
(2) Polysiloxane of General Formula (3) in which R_9 and R_{10} are methyl groups, and *para* bonds are formed at $n = 41$ and $b = 2$
(3) Polysiloxane of General Formula (3) in which R_9 and R_{10} are methyl groups, and *ortho* bonds are formed at $n = 101$ and $b = 3$
(4) Polysiloxane of General Formula (3) in which R_9 is a methyl group, R_{10} is a phenyl group, and *ortho* bonds are formed at $n = 41$ and $b = 3$
(5) Siloxane of General Formula (4) in which R_9 and R_{10} are methyl groups, and $n = 41$
*3 A blend of monomers (1)

[0036]

[Merits of the Invention] Because the injection molding obtained of the present invention is obtained from a polycarbonate-polysiloxane copolymer such that polysiloxane segments are selectively collected on the extreme surface (surface layer with a depth of less than 50 Å) in a concentration at least twice that of a core layer with a depth of 50 Å or greater, it is possible to achieve a surprising surface modification effect (to improve the lubricity, abrasion resistance, and other properties) of the polycarbonate injection molding with the aid of a small amount of polysiloxane. In addition, the injection molding pertaining to the present invention and consisting of a polycarbonate-polysiloxane copolymer possesses reduced clouding, better transparency, and more-sustainable mechanical characteristics (flexural, tensile, and the like) as a polycarbonate product than does an injection molding composed of a polycarbonate/polysiloxane mixture with a constant polysiloxane concentration.